

COLORED DISSOLVED ORGANIC MATTER IN SEDIMENTS AND SEAGRASS BEDS AND ITS IMPACT ON SHALLOW WATER BENTHIC OPTICAL PROPERTIES

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LONG TERM GOALS

The optical properties of shallow water coastal environments are a complex function of physical and biogeochemical processes occurring both in the sediments and in the water column. Developing models of the optical properties of these environments requires further knowledge of the processes affecting light alteration and modification by biogeochemical reactions in the surficial sediments and at the sediment-water interface. The goal of this proposal is to examine one aspect of this problem, namely the impact of dissolved organic matter (DOM) in sediment pore waters on benthic optical properties.

OBJECTIVES

I propose to examine the processes affecting the production of colored and fluorescent dissolved organic matter (CFDOM) in sediment pore waters, the mechanism(s) by which this material may be transported out of the sediments, and the impact of pore water CFDOM on the optical properties of the shallow water benthos (i.e., both the sediments, the sediment-water interface and the waters overlying the sediment, including the benthic boundary layer).

APPROACH

To address these questions I will use a combination of field measurements and experiments, all carried out in close cooperation and coordination with other funded CoBOP researchers. These include:

1. determining bottom water concentrations and sediment (pore water) profiles of CFDOM;
2. determining sediment profiles of other relevant solid phase and dissolved constituents (to characterize the basic biogeochemical properties of the sediments);
3. examining benthic fluxes of CFDOM using the core incubation techniques used in my previous NSF and ONR-funded studies (Burdige and Homstead, 1994; Burdige and Zheng, 1997; Skrabal *et al.*, 1997);
4. carrying out experiments to determine the “optical fate” of sediment CFDOM in the waters at or just above the sediment surface (i.e., once the pore water CFDOM is transported out of the sediments by any of the processes discussed above).

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In this project CFDOM from pore waters and bottom waters will be characterized both chemically and optically. Chemical analyses will involve measuring total dissolved organic carbon and nitrogen, using high temperature catalytic oxidation techniques that are routinely used in my lab. CFDOM will be characterized optically by measuring its UV/Vis absorption spectrum and its fluorescence excitation-emission spectrum. To further characterize CFDOM I will use high pressure size exclusion chromatography (HPSEC) coupled with UV/Vis and fluorescence detection. In previous studies, HPSEC has mainly been used with UV detection at 224 nm, to obtain the number- and weight-average molecular weights of the DOM compounds (e.g., Chin *et al.*, 1994). However in this aspect of this project the goal is to relate the optical properties of the CFDOM to its molecular weight distribution.

WORK COMPLETED

The work completed this year has involved developing the techniques that we will use in upcoming CoBOP field efforts in Monterey Bay and in the waters around Lee Stocking Island. These studies have been carried out in conjunction with on-going research funded through the ONR Harbor Processes Program (award no. N000149310899 to J. Donat and D. Burdige) and the NSF Chemical Oceanography Program (OCE-9302120 to D. Burdige; see **Related Projects** for further details). The work is being carried out by myself (as PI of the project), Mr. Kip Gardner (a research technician in my lab) and Dr. Wenhao Chen (a post-doctoral research associate hired for this project).

RESULTS

Sediment pore water samples from three contrasting sites in the Chesapeake Bay (sites M3, N3 and S3) and three sites along the mid-Atlantic shelf/slope break (sts. WC4, WC7 and AI) were studied using excitation-emission matrix (EEM) fluorescence spectroscopy (excitation wavelengths from 200 to 425 nm, emission wavelengths from 290 to 550 nm). The major fluorescence peaks observed in our samples appear to correspond to those observed in the water column. These included the “humic-like” fluorescence peaks A and C (excitation at about 250 and 350 nm and emission at about 410-470 nm) and the “protein-like” peaks U and T (excitation at about 225 and 275 nm and emission at about 305-375 nm). For all six sites, humic-like fluorescence increased with depth but at different rates. Samples from sites M3 and S3 were dominated by humic-like fluorescence and showed no (or weak) protein-like fluorescence. At the other sites (N3, AI, WC4, and WC7), protein-like fluorescence was dominant near the sediment surface, decreased with depth, and became less significant than humic-like fluorescence at depth (approx. 10 cm for st. N3 and 16 cm for the other three sites).

For most samples, peak A was stronger than peak C; in samples where protein-like fluorescence was observed, peak U was stronger than peak T. The ratio of peak A/peak C and that of peak U/peak T varied from around 0.8 to 2.5 with most values falling between 1.5 and 2.0. Peak C showed a much stronger correlation with pore water DOC than that observed with the other three peaks. The protein-like peaks U and T showed a much stronger correlation with DON than did the humic-like peaks A and C. For all of the sites a fairly good positive correlation was observed between the depth-average fluorescence intensity of peak C and sediment carbon oxidation rates;

a similar negative correlation was observed with peak T fluorescence and sediment carbon oxidation rates. For peaks A and C, the ratios of their fluorescence intensity to total DOC increased with depth. For peaks U and T, the ratios of their fluorescence intensity to total DON decreased slightly with depth. These observations suggest that humic-like fluorophores are produced and accumulate during the early diagenesis of sediment organic matter, while protein-like fluorophores are both produced and consumed during sediment diagenesis. These results will be presented at the up-coming Ocean Sciences meeting in San Diego (Chen and Burdige, 1997).

IMPACT

The fluorescence data collected so far will be useful in terms understanding the controls on DOM cycling in marine sediment pore waters (e.g., Burdige and Gardner, 1997), and in examining the extent to which coastal sediments are sources of CFDOM to coastal waters (the latter problem will be examined more directly in benthic flux studies to be carried out next month in Chesapeake Bay sediments). The work we have carried out this past year has also prepared us for up-coming CoBOP field efforts in Monterey Bay and in the waters around Lee Stocking Island.

TRANSITIONS

At the present time these results are not being utilized by others. However, this will likely change as we begin the joint CoBOP field efforts discussed above.

RELATED PROJECTS

As outlined above, work this year has been closely allied to an ONR project funded through the Harbor Processes Program (ONR award N000149310899, "Metal Complexing Ligands and Metal Speciation in Sediment Pore Waters: Implications for Sediment/Water Exchange and Water Column Metal Speciation", J. Donat and D. Burdige, co-PI's) and a recently-completed NSF funded project (OCE-9302120, "Fluxes of Dissolved Organic Matter from Marine Sediment", D. Burdige PI). These interactions have involved taking advantage of ship-time funded through our Harbor Processes project for the field work described here, and co-ordination of field sampling on these cruises to maximize the utilization of ancillary data relevant to all three projects.

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